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Evaluation of lattice parameter and defect related studies of $(KBr)_x(NaBr)_{1-x}$ mixed crystals grown from aqueous solution

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Abstract : Mixed crystals of KBr–NaBr of different compositions were grown by slow evaporation technique. Crystals were doped with gold. Both the undoped and gold doped crystals were γ-irradiated using ^{60}Co source. All the irradiated samples were subjected to thermoluminescence, optical absorption and ESR studies. The present study shows the composition dependence of the parameters and enhancement in the luminescence intensity as well as the absorption coefficient with gold doping. For the non-irradiated samples, lattice parameter determination, microhardness and dielectric studies have been carried out. Results of the studies are reported.

Keywords Mixed crystal, lattice parameter, microhardness, dielectric constant, thermoluminescence, optical absorption, electron spin resonance.

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1. Introduction

Mixed crystals have aroused considerable interest curiosity and have motivated extensive investigators because of wide applications. Among the well known mixed crystals, sixteen pairs of mixed alkali halides are completely miscible at room temperature and several have limited miscibility. The solid solutions of mixed alkali halides indeed constitute a very interesting study. There are several reasons for this choice. The location of the maxima of various colour center electronic bands for the mixed crystals, depends on the composition. So composition can be varied to suit any available laser wavelength in the appropriate region. In recent years, attempts have been made to use these crystals for optical information storage processes [1]. Some of the mixed crystals have found applications as Laser window materials [2,3] and as neutron monochromators [4].

In view of this, in the present study, alkali halide mixed crystal $(KBr)_x(NaBr)_{1-x}$ of different compositions were grown by slow evaporation technique from aqueous solution and various studies like determination of lattice parameter, microhardness, dielectric constant, thermoluminescence, optical absorption and electron spin resonance have been carried out on the grown mixed crystals.

2. Experimental

Mixed crystals of $(KBr)_x(NaBr)_{1-x}$ were grown by slow evaporation technique from aqueous solution. Well-defined optically transparent crystals were obtained for the composition x = 0.2, 0.4, 0.5, 0.7, 0.8 and 0.9. All combinations of mixed crystals were doped with Au^+ by diffusion technique [5,6].

The elemental analysis of the grown crystals were carried out by the energy dispersive X-ray (EDAX) spectroscopy. It is observed that the composition of the mixed crystal is not very different from the actual composition determined on the basis of the initial weights of the salts.

Grown crystals were cleaved and were subjected to γ-irradiation with ^{60}Co source to a strength of 10 Mrads.

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Irradiated samples were preserved in a black paper before subjecting them to optical absorption, electron spin resonance and thermoluminescence studies. The non-irradiated samples were subjected for the measurement of lattice parameter, microhardness measurement and dielectric constant measurement.

3. Results and discussion

3.1. Determination of lattice parameter :

The crystallinity of the crystals obtained was checked using the XRD pattern. The lattice parameter of the crystals was determined by a powder diffraction method. For this measurement, powder specimens were made by grinding the crystals. The powder was then mounted on glass slides in a wax matrix. Diffraction patterns were recorded using computer controlled powder X-ray diffractrometer with CuK_α (λ = 1.5418 Å) as a target. Typical 2θ scan range was made from 20 to 80° and the scan speed was 2° per minute. All diffraction patterns were recorded at room temperature

The values of the lattice parameter of mixed crystals $(KBr)_x(NaBr)_{1-x}$ have been estimated using the Vegard's law [7]. Figure 1 shows the plot of composition *versus* lattice parameter. There is good agreement between the experimental and theoretical values of lattice parameters. This has been justified by comparing the values shown in Table 1.

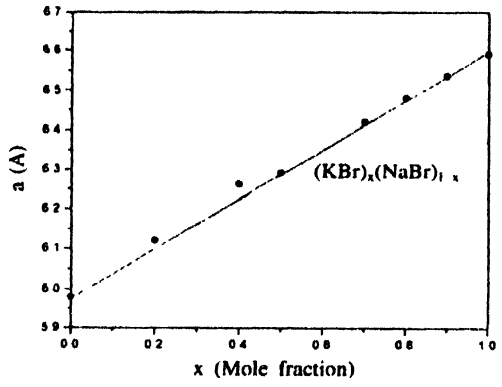

Figure 1. Variation of lattice constant with the mole fraction (x) in case of $(KBr)_x(NaBr)_{1-x}$. Solid circles represent the experimental values while the line is drawn through the calculated values assuming Vegard's law.

Table 1. Lattice parameters of $(KBr)_x(NaBr)_{1-x}$ mixed crystals.

Mole % KBr	Lattice parameter in Å (experiment)	Lattice parameter in Å (from Vegard's law)
0	5.98	5.98
20	6.12	6.101
40	6.261	6.225
50	6.291	6.287
70	6.42	6.411
80	6.479	6.472
90	6.537	6.534
100	6.59	6.59

3.2. Microhardness studies :

Microhardness measurements were carried out using Zwick 3212 hardness tester fitted with a Vicker's diamond pyramidal indenter. All the indentation measurements were carried out on the freshly cleaved samples. The indentation was made at a load of 50P and the time of indentation was kept at 10 sec. The indentated impressions were approximately square. The crystal surfaces were indented at different sites. Diagonal lengths of the indented impressions were measured using calibrated micrometer attached to the eyepiece of the microscope. Several indentations were made on each sample. The average value of the diagonal length of the indentation mark was used to calculate the hardness.

The Microhardness is calculated using the expression [8]

$$H = 1.8544\ P/d^2\ \text{Kg mm}^{-2},$$

where P is the applied load in Kg and d the average diagonal length of the Vickers impression in mm after unloading.

Figure 2 shows the variation of microhardness with composition for undoped and Au^+ doped KBr–NaBr mixed systems.

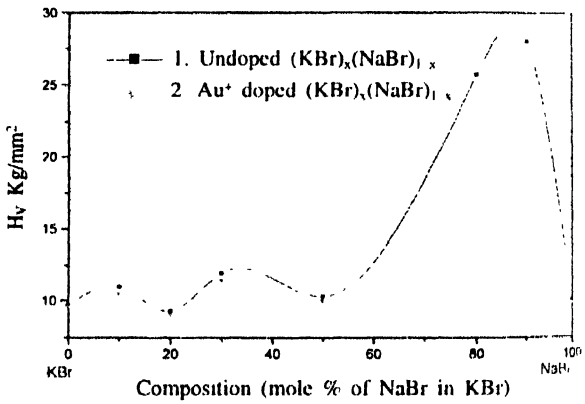

Figure 2. Variation of microhardness with composition in (1) undoped $(KBr)_x(NaBr)_{1-x}$, (2) Au^+ doped $(KBr)_x(NaBr)_{1-x}$ mixed crystals

It is observed that the formation of a mixed crystal is accompanied by an increase in hardness and microhardness varies non-linearly with composition. Although hardness has been defined in several ways, it is now generally accepted that it is the resistance offered to dislocation motion. There are several contributions to the resistance to the dislocation motion and they can be classified into two types (i) the intrinsic resistance which depends on some structure insensitive physical parameter of the crystal and (ii) disorder parameter which depends on the concentration of the imperfections.

The non-linear variation of microhardness with composition is due to the presence of imperfections. These imperfections can be vacancies, impurity-vacancy pairs, dislocations, low-angle grain boundaries *etc.* The studies

made by others on ionic conductivity of mixed crystals [9] show that conductivity is high for mixed crystals as compared to the end crystals. Since ionic conductivity is solely due to the presence of charged vacancies, these results therefore indicate that mixed crystals contain excess of vacancies. The results on dislocation morphology [10] shows that the low-angle grain boundaries and dislocations are more in mixed crystals compared to pure crystals. Also Tiller's eutectic crystallization mechanism may be responsible for the origin of low-angle grain boundaries in mixed crystals [11]. Thus vacancies, dislocations and grain boundaries appear to be the dominant imperfections in mixed crystals and these may be responsible for the observed non-linear variation of microhardness in them.

It is well known that lattice strains are developed in mixed crystals due to the difference in the size of the atoms or ions. The size of different ions is shown in the table below [12].

Pauling ionic radii in Å

Ion	Ionic size Å
Br^-	1.95
K^+	1.33
Na^+	0.95

Therefore internal strain arising out of the difference in ionic sizes, may be responsible for the formation of various types of imperfections such as vacancies, dislocations, low angle grain boundaries and other defects, which in turn, were responsible for the non-linear variation of microhardness. The results also suggest that the microhardness in mixed crystals depends upon the difference in the size of the ions and not on the nature of the ions substituted.

Microhardness of Au^+ doped crystals is less than the undoped one. It implies that the monovalent impurity ions (Au^+ ions) are not favouring the hardness, which is in agreement with the earlier reports.

3. Dielectric studies :

The samples were ground to proper thickness and polished. The final dimensions of the samples were about 1.5 to 2 cm and 0.1 to 0.3 cm in thickness. Each sample was electroded on either side with air-drying silver paste so that behaved like a parallel plate capacitor. A 4275A, multi frequency LCR meter (Hewlett-Packard) was used to measure capacitance (C) and dissipation factor (D) of the sample as a function of frequency. The dielectric constant (ε') and dielectric loss ($\tan\delta$) were calculated from C and D using the relations :

$$\varepsilon' = \frac{Cd}{A\varepsilon_0} \quad \text{and} \quad \tan\delta = D\varepsilon',$$

where C is the capacitance of the sample, d the thickness of the sample, A the area of the face in contact with the electrode and ε_0 the permittivity of free space.

The variation of dielectric constant on composition is shown in the Figure 3. It is observed that the dielectric constant varies non-linearly with composition.

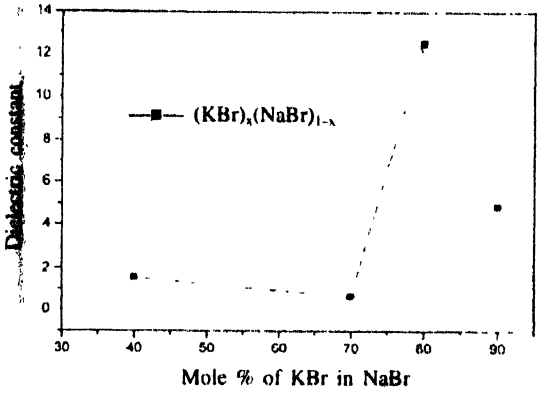

Figure 3. Variation of dielectric constant with composition in $(KBr)_x(NaBr)_{1-x}$ mixed crystals

The variation of dielectric constant (ε') with frequency at room temperature for the undoped and Au^+ doped mixed crystals are shown in the Figures 4 to 5. It is observed that the value of dielectric constant is more at lower frequency.

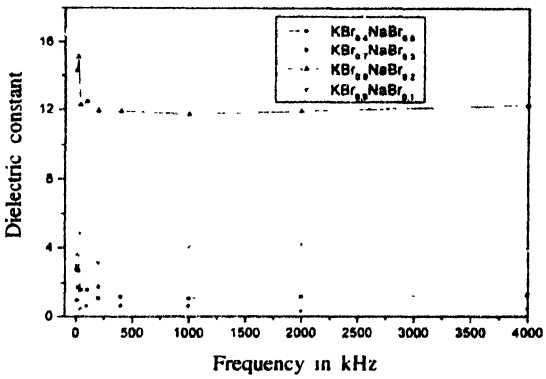

Figure 4. Variation of dielectric constant with frequency in undoped $(KBr)_x(NaBr)_{1-x}$ mixed crystals

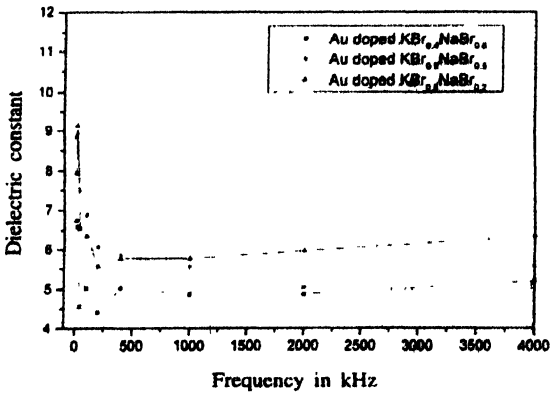

Figure 5. Variation of dielectric constant with frequency in Au^+ doped $(KBr)_x(NaBr)_{1-x}$ mixed crystals.

It decreases with increasing frequency. The dielectric loss is very large at low frequency but falls to moderately low values at higher frequencies.

Generally, the dielectric constant of a material is related to electronic, ionic, dipolar and space charge polarization. All these are active at low frequencies. In fact, the nature of variation of dielectric constant with frequency indicates the type of polarization present.

The space charge contributions will depend on the purity and perfection of the crystals. Its influence is negligible at very low temperatures and is noticeable in the low frequency region. The dipole orientational effect can sometimes be seen in some materials even upto 10^{10} Hz. The ionic and electronic polarizations always exist below 10^{13} Hz.

Recollecting our data, the larger values of dielectric constant at low frequencies may be ascribed to space charge polarizations due to charged defects in the material. This is supported by the fact that $\tan\delta$ has very large values at low frequencies and also the $\tan\delta$ varies as $1/f$ indicating that it is due to D.C. conduction.

3.4. Thermoluminescence studies :

γ-Irradiated undoped/Au^+ doped mixed crystals were subjected to the TL studies. In this study, a previously excited sample is heated at an uniform rate from low temperature to high temperature and the luminescent intensity emitted by the sample is recorded using home-made experimental set up where the radiation is converted to electric current by a 931A photomultiplier tube.

In KBr–NaBr mixed crystals, a prominent characteristic glow peak is observed in the range 438–480 K and there is a non-linear shift in the glow peak and trap depth with composition. These peaks are shown to be mainly due to the destruction of *F*-centers.

Similar pattern of the glow peaks were observed in Au^+ doped KBr–NaBr mixed crystals in all combinations, whereas the thermoluminous intensity is more in the gold doped mixed crystals.

The glow curves which are originated from the recombination of thermally released charge carriers from the trap at luminescent center obtained for all composition of mixed crystals, were analyzed by numerical curve fitting [13,14] and the trap depth (activation energy) has been calculated. The thermoluminescence glow curves of undoped and Au^+ doped KBr–NaBr crystals are shown in the Figures 6 and 7 and the computed values of the trap depth are given in the Tables 2 and 3 respectively.

3.5. Optical absorption studies :

Optical absorption spectra of the irradiated crystals were recorded using the Hitachi U-3200 spectrophotometer in the range 200–800 nm at room temperature. The sample holder in the spectrophotometer, originally designed for liquids, was modified to accommodate thin plates of crystals.

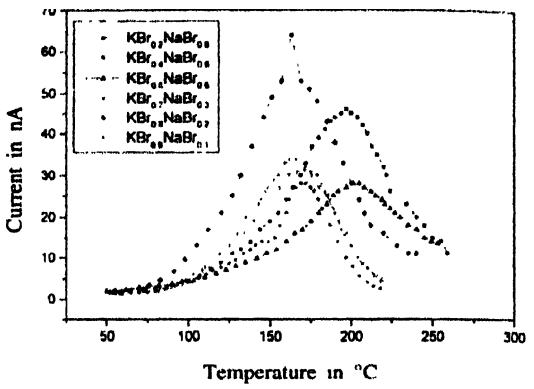

Figure 6. Thermoluminescence glow curve of undoped $(KBr)_x(NaBr)_{1-x}$ mixed crystals irradiated with a dosage 10 Mrads.

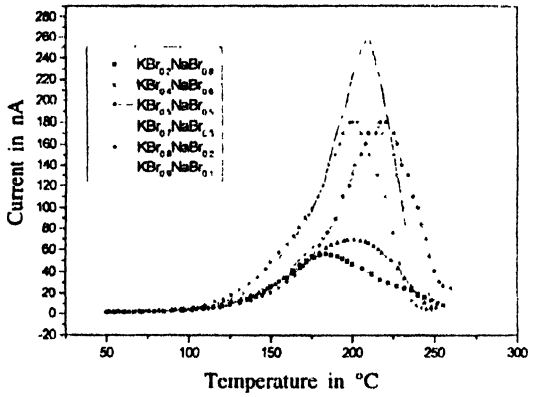

Figure 7. Thermoluminescence glow curve of Au^+ doped $(KBr)_x(NaBr)_{1-x}$ mixed crystals irradiated with a dosage 10 Mrads.

Table 2. Estimated values of trap depth of undoped $(KBr)_x(NaBr)_{1-x}$ mixed crystals irradiated with a dosage 10 Mrad.

Concentration (x)	Glow peak	Tg (K)	Trap depth (eV)
x = 0.2	Strong	470	1.3154
x = 0.4	Strong	443	1.2459
x = 0.5	Strong	476	1.33
x = 0.7	Strong	442	1.2337
x = 0.8	Strong	436	1.2155
x = 0.9	Strong	438	1.2293

Table 3. Estimated values of trap depth of Au^+ doped $(KBr)_x(NaBr)_{1-x}$ mixed crystals irradiated with a dosage 10 Mrad.

Concentration (x)	Glow peak	Tg (K)	Trap depth (eV)
x = 0.2	Strong	457	1.2791
x = 0.4	Strong	473	1.3243
x = 0.5	Strong	472	1.3203
x = 0.7	Strong	486	1.3607
x = 0.8	Strong	491	1.3719
x = 0.9	Strong	483	1.3604

The accuracy in the measurement of the absorption coefficient was 0.001. Using Abbe's refractometer, the refractive index n has been determined accurately for all combinations with accuracy of 0.001, which is required in the calculation of density of defects.

The absorption spectra of KBr–NaBr mixed crystals showed weak absorption V_1 band in the range 350–380 nm and F band around 625 nm. α-band is observed in some combinations around 230 nm. By exchanging the cations, F band peak position remains unchanged with the composition whereas V_1 band drifts between KBr and NaBr. The half bandwidth has varied non-linearly with composition and attained maximum value for the composition 80 mole percent NaBr in KBr.

In the Au^+ doped KBr–NaBr mixed crystals of all the combinations, similar absorption pattern is observed as in the undoped one and the absorption coefficient of doped one was observed to be more.

α-band appears to be due to a perturbation of the fundamental lattice absorption of the crystal by the presence of the F-center. Perturbation is due to a negative ion vacancy. Hence, it can be concluded that the anion vacancies are responsible for the occurrence of the α-band. The low value of the absorption coefficient of this band is an indication of the concentration of such defects being small in these samples.

Broadening of F-band has been observed in KBr–NaBr mixed crystals compared to the pure components. Accordingly, half band width is observed to be greater.

The broadening of the F-band can be attributed to the superposition of seven elementary bands corresponding to seven different combinations of the two cations which surround the F-center octahedrally [15]. It is also due to the additional effect of Schottky defects [16].

Increase in half width of the F-band is a result of superposition of the absorption due to the centers having different number of anions bordering the F-center.

The absorption spectra of the irradiated mixed crystals are shown in the Figures 8 and 9. The computed F-center

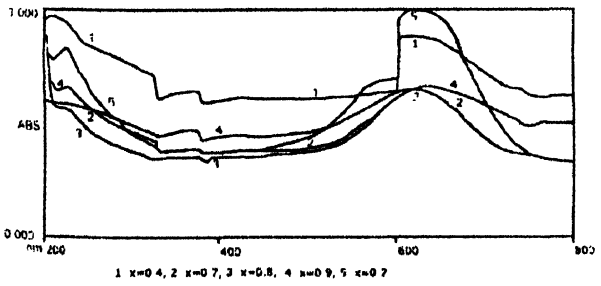

Figure 8. Optical absorption spectra of undoped $(KBr)_x(NaBr)_{1-x}$ mixed crystals irradiated with a dosage 10 Mrads.

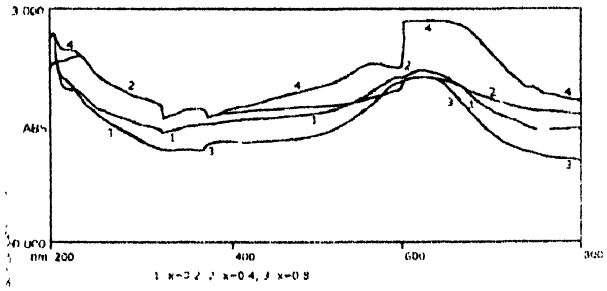

Figure 9. Optical absorption spectra of Au^+ doped $(KBr)_x(NaBr)_{1-x}$ mixed crystals irradiated with a dosage 10 Mrads.

density determined using equation of Smakula *et al* [17], is found to be around 10^{17} centers/cm^3 and are tabulated in Table 4.

Table 4. Half band width and colour center density of $(KBr)_x(NaBr)_{1-x}$ mixed crystals irradiated with a dosage 10 Mrads.

Sample	Refractive index	Peak position (nm)	Absorption coefficient	Half band width (ev)	Density of defects (10^{17} cm^{-3})
$(KBr)_{0.2}(NaBr)_{0.8}$	1.5969	230	2 644	18.719	5 7936
		625	3 171	14 0393	5.2114
$(KBr)_{0.4}(NaBr)_{0.6}$	1 5811	370	1 918	–	–
		452	1.813	–	–
		621	2.607	8.4791	2.6195
$(KBr)_{0.7}(NaBr)_{0.3}$	1.5588	371	1 14	–	–
		625	1.915	8.8098	2.0338
$(KBr)_{0.8}(NaBr)_{0.2}$	1.5492	362	1 057	–	
		626	1 952	9.3609	2.219
$(KBr)_{0.9}(NaBr)_{0.1}$	1.5427	367	1 407	–	–
		633	1 945	3 9066	9 2733
Au^+ doped	1.5938	372	1.688	–	–
$(KBr)_{0.2}(NaBr)_{0.8}$		625	2 114	5.2859	1.3898
$(KBr)_{0.4}(NaBr)_{0.6}$	1 5802	626	2.186	5.1543	1.3352
$(KBr)_{0.7}(NaBr)_{0.3}$	1.5548	625	2.179	8 8098	2.3142
$(KBr)_{0.8}(NaBr)_{0.2}$	1.5447	235	2 757	10.0176	3.354
		372	2 002	–	–
		571	2.64	–	–
		631	3.314	6.0009	2.415

3.6. Electron spin resonance studies :

The ESR spectra were recorded using the Bruker X-band ESR (ER200D) spectrometer. All the irradiated samples were subjected to ESR study. Samples possessing paramagnetic property have given rise to good ESR derivative. From the resonance signal, g value have been calculated which gives information regarding the chemical environment. The results are tabulated in Table 5. The signal is more pronounced in Au^+ doped crystals.

Table 5. Estimated values of g from the ESR spectra.

Sample	Composition	g value
$(KBr)_x(NaBr)_{1-x}$	$x = 0.4$	2.0877
	$x = 0.8$	2.0413
Au^+ doped $(KBr)_x(NaBr)_{1-x}$	$x = 0.2$	2.1532
	$x = 0.8$	2.2189

4. Conclusions

Good optically transparent mixed alkali halide crystals $(KBr)_x(NaBr)_{1-x}$ of different composition, were grown by slow evaporation from aqueous solution.

Elemental analysis have been confirmed by EDAX.

There is good agreement between the experimentally determined values of the lattice parameter with the theoretical values obtained using Vegard's law.

Microhardness has varied non-linearly with composition.

Microhardness is more in mixed crystals than in the pure components for higher composition of NaBr. The increase in hardness in mixed crystals has been attributed to the internal strains arising out of the difference in ionic sizes which is responsible for the formation of dislocations, low-angle grain boundaries and other defects.

Monovalent impurity ions (Au^+ ions) are not favoring the hardness in agreement with the earlier results.

The value of the dielecric constant in mixed KBr–NaBr crystals is more than the pure components. Dielectric constant varies non-linearly with composition. Large value of dielectric constant at low frequencies in the present study confirms the purity of the sample, secondly, as due to the space charge polarization. Dielectric constant is highest for the composition $KBr_{0.8}$ $NaBr_{0.2}$ for all the frequencies up to 4 MHz due to the considerable differences in ionic sizes as well as higher Van der Waals contribution to the lattice energy [18].

The glow peaks observed in all the combinations of KBr–NaBr mixed crystal are mainly due to the destruction of the F-centers.

Broadening of F-band is observed in the KBr–NaBr mixed crystals compared to pure components. F-band peak position and the half band width of the F-center has answered for compositional dependence.

Luminous intensity as well as absorption coefficient are more in samples containing Au^+ ions indicating the role of Au^+ ions.

Resonance signals are pronounced in Au^+ doped crystals compared to undoped one depicting the higher paramagnetic property in the sample.

Acknowledgments

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